

On the Spin Gap Phase in

$$\lambda\text{-(BETS)}_2\text{GaX}_z\text{Y}_{4-z}$$

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The nature of the insulating ground state in quasi-two-dimensional organic conductor $\lambda\text{-(BETS)}_2\text{GaX}_z\text{Y}_{4-z}$, where the existence of a spin gap is suggested by susceptibility measurement, has been studied theoretically. Hartree-Fock calculations at absolute zero temperature show that if the on-site Coulomb interaction exceeds some critical value, then antiferromagnetic spin ordering emerges and eventually leads to an insulating state which can be considered as a two-dimensional localized spin system. Based on the quantum Monte Carlo simulations of Katoh and Imada, we will show that this system locates near the boundary between the antiferromagnetic phase and the spin gap phase, so that experimental facts can be explained.

KEYWORDS: BETS, spin gap, Hartree-Fock approximation, on-site Coulomb interaction, antiferromagnetic spin ordering

Organic conductors made of BEDT-TSeF (bisethylenedithiotetraselenafulvalene, abbreviated as BETS), which is a seleno-analog of the well-known BEDT-TTF (abbreviated as ET), have two-dimensional (2D) character as ET compounds does. Among them, a new series of superconductors $\lambda\text{-(BETS)}_2\text{GaX}_z\text{Y}_{4-z}$ (X,Y=F,Cl,Br) exhibit interesting electronic properties. By recent resistivity and magnetic susceptibility measurements with different z -values and different pressures, the phase diagram of $\lambda\text{-(BETS)}_2\text{GaX}_z\text{Y}_{4-z}$ was proposed¹⁾ as shown in Fig. 1. The substitution of X and Y to smaller atoms, the decrease of the z -value when X is a larger atom than Y or condition of applied pressure corresponds to the reduction of the unit cell volume V . Since the magnetic susceptibility¹⁾ showed a steep decrease without anisotropy by lowering the temperature in the compounds that exhibit an insulating ground state, this phase, which is next to the superconducting phase, is considered to be a nonmagnetic insulating (NMI) phase. We can see that the general feature of this phase diagram is analogous to the proposed phase diagram of $\kappa\text{-(ET)}_2\text{X}$,²⁾ where the 10-K superconducting phase is situated near the Mott antiferromagnetic insulating (AFI) phase,³⁾ if the NMI phase in the present case is replaced by the AFI phase.

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Fig. 1. Experimental phase diagram of λ -(BETS) $_2$ GaX $_z$ Y $_{4-z}$ on the plane of unit cell volume (V) and temperature (T).¹⁾ NMI, SC, PI and PM stands for the nonmagnetic insulating, superconducting, paramagnetic insulating and paramagnetic metallic phases, respectively.

λ -(BETS) $_2$ GaX $_z$ Y $_{4-z}$ consists of four BETS molecules in a unit cell and take layered structure of 2D BETS network, whose structure in the donor plane is schematically shown in Fig. 2. It is seen in Fig. 2 that there exist dimers (1–2) and (3–4) which are symmetrically equivalent since their intradimer transfer integral t_A is twice as large as the others. We note that values of t_B and t_C differ due to the crystal structure. BETS is electrically expressed as BETS $^{+1/2}$ in this family, and then there are two holes in a unit cell. The extended Hückel band calculations¹⁾ predict that these λ -type compounds are metallic with a 2D Fermi surface very similar to those of the κ -type conductors, despite their large differences in the molecular arrangement. The partially-filled higher two bands and the fully-occupied lower two bands are separated so we can consider the system effectively half-filled, thus strong correlation can lead the system to a Mott insulator. Since the behavior in the magnetic susceptibility in the insulating state is reminiscent of that in the quasi-one-dimensional organic spin-Peierls compounds such as (TMTTF) $_2$ PF $_6$ ⁴⁾ which also has an effectively half-filled band, we may speculate that the NMI phase is due to the spin-Peierls transition which is characteristic of one-dimensional materials, yet the 2D character of these BETS compounds may contradict this conjecture. Our aim in this paper is to clarify the origin of this NMI phase.

In order to study the electronic structure of these BETS salts, we only consider their 2D donor plane (Fig. 2) which consists of transfer integrals between BETS molecules and the on-site Coulomb interaction U on BETS molecule. The Hamiltonian is written as

Fig. 2. A schematic view of the structure of the donor plane in λ -(BETS) $_2$ GaX $_z$ Y $_{4-z}$. The values of transfer integrals for Y=Cl, $z = 0$ are given by $t = Es$, where s is the value of the overlap integral from ref. 1 and $E = -10\text{eV}$.

$$H = \sum_{\langle i,j \rangle} \sum_{\sigma} \left(t_{i,j} a_{i\sigma}^{\dagger} a_{j\sigma} + h.c. \right) + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (1)$$

where $\langle i, j \rangle$ denotes the neighbor site pair, σ is a spin index which takes \uparrow and \downarrow , $n_{i\sigma}$ and $a_{i\sigma}^{\dagger}$ ($a_{i\sigma}$) denote the number operator and the creation (annihilation) operator for the electron of spin σ at the i th site, respectively.

We treat U in the Hartree-Fock (HF) approximation, as in ref. 3, and assume that the periodicity of the electron system along the a -direction is the same as that of the original lattice. As for the c -direction, we considered two cases; one with the same periodicity as that of the original lattice system, i.e. the paramagnetic or ferromagnetic solutions along the c -direction, or one two-fold that of the original lattice system, i.e. the antiferromagnetic solution along the c -direction. Thus, there are four or eight different sites in a unit cell and the HF Hamiltonian in k -space is given by

$$H^{HF} = \sum_{k\sigma} \begin{pmatrix} a_{1k\sigma} \\ a_{2k\sigma} \\ \vdots \\ a_{mk\sigma} \end{pmatrix}^{\dagger} \left[h_0 + U \begin{pmatrix} n_{1\bar{\sigma}} & & 0 \\ & n_{2\bar{\sigma}} & \\ & & \ddots \\ 0 & & & n_{m\bar{\sigma}} \end{pmatrix} \right] \begin{pmatrix} a_{1k\sigma} \\ a_{2k\sigma} \\ \vdots \\ a_{mk\sigma} \end{pmatrix}, \quad (2)$$

where $m = 4$ or $m = 8$ according to the unit cell size, $\bar{\sigma}$ is opposite to σ and $a_{\nu k\sigma}$ is the Fourier transform of $a_{i\sigma}$, i.e. $a_{\nu k\sigma} = \frac{1}{\sqrt{N_{\text{cell}}}} \sum_{\alpha} e^{iR_{\alpha\nu}k} a_{(\alpha\nu)\sigma}$ and N_{cell} is the total number of unit cells. α and ν denote the cell number and the number of the molecule, respectively. The h_0 term is a matrix which comes from the first term of eq. (1) and is diagonalized to lead to almost the same dispersion as that given by the extended Hückel band calculation.¹⁾

In eq. (2), the electron densities for each spin, $n_{\nu\sigma}$ ($\nu = 1, 2, \dots, m$ and $\sigma = \uparrow, \downarrow$), are determined self-consistently by

$$n_{\nu\sigma} = \frac{1}{N_{\text{cell}}} \sum_k \langle a_{\nu k\sigma}^\dagger a_{\nu k\sigma} \rangle. \quad (3)$$

They are calculated together with the equation for the Fermi energy implicitly given by

$$N_e = \sum_{\nu\sigma} n_{\nu\sigma}, \quad (4)$$

where N_e is the total number of electrons in the unit cell in the highest occupied molecular orbital (HOMO) levels. ($N_e = 6$ for $m=4$ or $N_e = 12$ for $m=8$ in the system currently considered.)

The calculations indicate that an antiferromagnetic (AF) order appears when U exceeds some critical value and it affects the degree of the band overlap. The calculated absolute magnitude of spin moment, S_z , for molecules 1 and 2 and the band gap as a function of U are shown in Fig. 3. We use the term ‘band gap’ as a value of the lowest amount of energy for the highest (second) partially or fully filled band minus the highest amount of energy for the second (third) partially or fully filled band for $m=4$ ($m=8$), so a negative band gap implies a finite band overlap. The results indicate that there exist two phase transitions; a 2nd-order transition between a paramagnetic metal state and an AF metal (AFM) state at $U = U_c \simeq 0.279$ eV and another 2nd-order transition from AFM state to AFI state at $U = U_{MI} \simeq 0.296$ eV. The hole density at each site is slightly different from +0.5 but is similar. In the AFM and AFI phases, the configuration of spin alignments is shown in the inset of Fig. 3. The direction of the spin moments inside the dimers are the same and a 2D AF ordering occurs between dimers. We note that $S_z(1) = -S_z(4)$, $S_z(2) = -S_z(3)$ in each row along the a -direction, and that $S_z(1)$ and $S_z(2)$ differ by a few % mainly due to the differences of the transfer integrals t_B and t_C .

One can extract the essence by taking each dimer as a unit together with the effective overlap integrals between dimers. This view is called the dimer model in the case of κ -(ET)₂X.^{2,3)} The above results show that in the large U region, where the BETS compounds are considered to be located, the system can be viewed as a 2D localized spin system, therefore, we can construct an effective 2D Heisenberg spin model as schematically shown in Fig. 4. We estimate the superexchange coupling constants, J , using the relation $J \simeq 4t^2/U_{\text{dimer}}$ (Note that U_{dimer} is the effective Coulomb interaction between two holes in a dimer), and conclude that the magnitudes of the interactions between the spins are $J_C \simeq 0.52J_B$, $J_\perp \simeq 0.72J_B$, $J_s \simeq 0.19J_B$ and $J_t \simeq 0.02J_B$. If we neglect J_s and J_t , which are noticeably smaller than the others, the system can be viewed as dimerized AF Heisenberg chains along the a -direction coupled by interchain coupling J_\perp by which the Hamiltonian is described as

$$\begin{aligned} H = & J_B \sum_{i \text{ even}} \mathbf{S}_i \cdot \mathbf{S}_{i+\hat{a}} + J_C \sum_{i \text{ odd}} \mathbf{S}_i \cdot \mathbf{S}_{i+\hat{a}} \\ & + J_\perp \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+\hat{c}}, \end{aligned} \quad (5)$$

Fig. 3. U dependence of the absolute magnitude of spin moments, S_z , and the band gap (negative value implies a band overlap).

where \mathbf{S}_i is the $S = 1/2$ spin operator on the i th site and \hat{a} and \hat{c} denote the unit vector in the a -direction and the c -direction, respectively.

In 2D quantum spin systems, quantum fluctuations, which we have not taken into account until now, result in the competition between the antiferromagnetic ordered state and the disordered spin liquid state which has a spin gap. In our model there are two key parameters which determine which state will be realized; the degree of dimerization, i.e. the difference between J_C and J_B , and the interchain coupling J_\perp . As a general tendency, the spin gap phase is stabilized in the region where the degree of dimerization is large enough. The interchain coupling J_\perp prefers the AF state when $J_\perp \lesssim J_C, J_B$. In our system, however, $J_\perp \sim J_C, J_B$ and it is not obvious which state is stabilized. Katoh and Imada⁵⁾ carried out quantum Monte Carlo simulations to the Hamiltonian (5), and determined the phase diagram in a parameter space of the magnitude of interchain coupling and the degree of dimerization (in their notation $J_B = J(1 + \delta)$ and $J_C = J(1 - \delta)$, δ : degree of

Fig. 4. Effective 2D Heisenberg model for localized spins in the dimer model for λ -(BETS)₂GaBr_xCl_{4-x}.

dimerization). According to their results, our spin system is located in the region close to the boundary between the AF phase and the spin gap phase, but slightly in the region of the AF state. It is expected that J_s , which has been neglected so far, pushes the system toward the spin gap phase. Considering the magnetic susceptibility experiments,¹⁾ the NMI phase of λ -(BETS)₂GaX_zY_{4-z} is then thought to be in the spin gap regime.

We can either see the system as 2-leg ladders along the c -direction whose interaction along the rungs is J_B and that along the legs is J_\perp , coupled by interladder coupling J_C . Recently, a similar system, where two-leg ladders are coupled three-dimensionally, was studied.^{6,7)} For example, in LaCuO_{2.5},^{8,9,10)} the static susceptibility⁸⁾ suggests a spin liquid state with a spin gap, while NMR⁹⁾ and μ SR¹⁰⁾ measurements indicate transition to a magnetically ordered phase. Theoretical studies^{6,7)} indicate that in a system located in the AF phase near the transition point to the spin liquid state, the static susceptibility has the form $\chi(T) = \chi_0 + aT^2$, with a small χ_0 which will not be identified easily by experiment. Therefore, we cannot exclude the possibility that λ -(BETS)₂GaX_zY_{4-z} is such an unconventional AF, close to the quantum critical point. For the moment we cannot decide between the two possibilities, the 2D spin-gap phase or the AF close to criticality, and must wait for further experiments, such as NMR and μ SR measurements for clarification.

Increasing J_C corresponds to the decrease of the degree of dimerization in the picture of dimerized Heisenberg chains, and to the increase of the interladder coupling in the picture of ladders system. In either picture, we see that, if J_C increases, the system moves in the direction of the AF ordered state. Therefore, if one can synthesize compounds analogous to λ -(BETS)₂GaX_zY_{4-z}, but with a smaller degree of dimerization, the system should have AF ground state. By controlling the systems in such a way, we will be able to study quantum spin systems systematically.

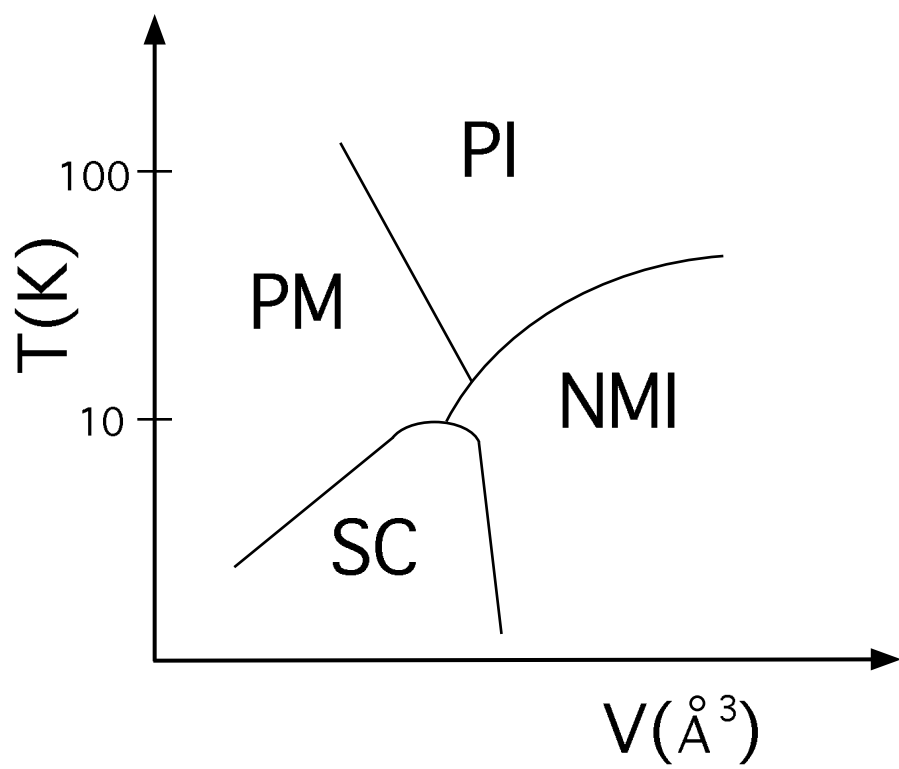
In summary, we have studied the nature of the nonmagnetic insulating phase in λ -(BETS)₂GaX_zY_{4-z}. Hartree-Fock calculations suggest that the on-site Coulomb interaction U causes an AF insulating state, which is a Mott insulator with one hole per dimer. Deducing from

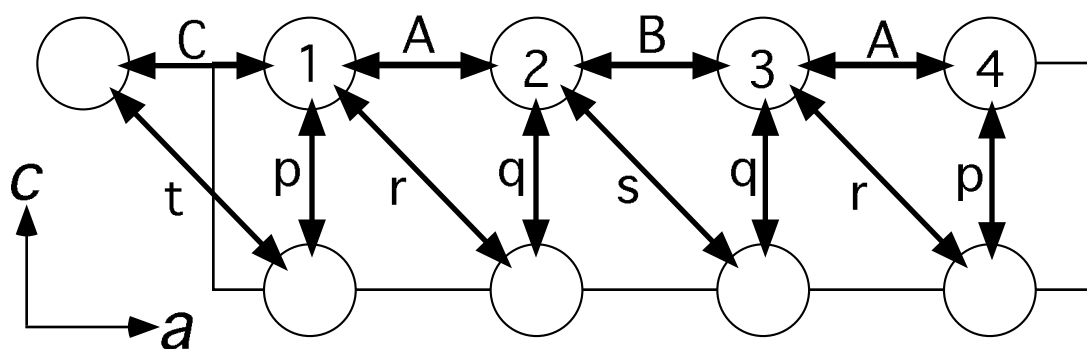
these results, we constructed an effective 2D localized dimer spin model with different exchange couplings. It is argued that quantum effects make this system a disordered spin liquid state with a spin gap, and we infer that the system is located close to the quantum critical point.

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t_A 0.274 eV
 t_B 0.111 eV
 t_C 0.080 eV

t_p -0.021 eV
 t_q -0.040 eV
 t_r 0.034 eV
 t_s 0.049 eV
 t_t 0.0065 eV

